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14. ABSTRACT

The intent of this program was to investigate whether the deposition of transition metal carbides could improve the performance of field emitter array cathodes for use in field emitter flat panel displays. Both zirconium carbide and hafnium carbide were studied, either by deposition onto prefabricated arrays with molybdenum emitters (film on emitter) or by deposition into apertures in "blank" arrays , thereby forming solid emitters of the carbides. The film on emitter technique proved successful, reducing the turn-on voltage necessary for cathode operation and producing more stable emitter operation. The solid cone technique did work, but was much harder to control and make reproducible.

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Final Technical Report
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Development of Transition Metal Carbide Field Emitters for Use in FEA Display Systems

Submitted to
Office of Naval Research

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I. Introduction

The purpose of this research program was to develop field emitter arrays (FEAs) with carbide film coated emitters and with solid carbide emitters, for use as stable, low-voltage cathodes for field emission displays (FEDs). We proposed to examine the suitabilities of the two transition metal carbides zirconium carbide (ZrC) and hafnium carbide (HfC) for these applications. Since our expertise was in the area of surface physics of carbide materials and in field emission theory and experiment, but not in the fabrication of FEA structures, we proposed to modify FEA structures provided by the FEA suppliers MCNC and SRI. These were to be obtained in two forms: 1) with molybdenum (Mo) or silicon (Si) emitters onto which carbide films would be overcoated, and 2) with apertures only but no emitters ("blank arrays") into which solid carbide emitters would be deposited.

II. Experimental techniques

A. Carbide film characterization

The first and most fundamental part of the project was the characterization of ZrC and HfC films deposited onto substrates of Mo and Si. This work allowed us to develop and calibrate the deposition process, study film-substrate interactions, and characterize important parameters of the deposited film, including work function and resistance to contamination.

B. Carbide film deposition on FEAs

Most of the program effort was devoted to the development of reproducible films deposited onto Mo field emitters in FEAs provided by SRI. The basic idea was to obtained a pre-tested FEA sealed in a vacuum environment, remove it from the packaging and install it into our vacuum system, and perform I-V testing to reaffirm the initial operating characteristics of the FEA. Then a film was deposited, and the emitter was again tested to see if there was an improvement in operation. Sequentially thicker and thicker films could be deposited onto the FEA, with I-V testing between depositions, in order to determine changes in operating characteristics as a function of film thickness. The FEA could also be exposed to controlled contaminant gases or ambient atmosphere and then retested, or it could be operated under controlled contaminant gas pressures. These various experimental techniques allowed us to evaluate improvements in emitter performance due to the carbide film under ideal vacuum conditions, the effects of exposure to contaminants on subsequent operation of carbide-coated emitters, and the potential for operation of these emitters in poor vacuum conditions.

C. Solid carbide emitter fabrication in blank arrays

The preparation of solid carbide emitters in FEAs involved more complicated preparation than carbide deposition onto Mo emitters. We obtained blank arrays either from SRI or by fabrication of our own structures using focused ion beam microfabrication equipment located at FEI Company. Then, in collaboration with Capp Spindt of SRI, we developed techniques for deposition of insulating, liftoff and conducting layers to mimic the proprietary process which SRI has developed, but to make it compatible with deposition of carbide emitters. A significant amount of effort was devoted to this development. Several difficulties were encountered, but the most significant was the problem of getting the carbide emitter cones to stick to the Si substrate material without moving off center in the FEA apertures during wet chemistry processing. Testing of the FEAs thus prepared was similar to that described for film-coated emitters, but also included a significant amount of scanning electron microscopy (SEM) to study the morphologies of the deposited emitter cones.

III. Results

A. Carbide coated Mo emitter FEAs

Deposition of carbide films onto prefabricated field emitter arrays proved to be advantageous. Emitter work functions were reduced by a significant amount, startup voltages were reduced, and stability of operation was improved. Table I shows a summary of pertinent work function reduction results for deposition of ZrC or HfC onto carefully prepared individual emitters of W, Mo, or Si, as well as for deposition onto FEAs.

TABLE I
Work Function Reduction by Carbide Deposition

Film type & Substrate	Voltage Reduction @ same current	Work Function Ratio from F-N	Work Function Clean (eV)	Work Function with Film (eV)
ZrC/W	38%	0.78	4.52	3.54
ZrC/Mo	56%	0.64	4.60	2.95
ZrC/Si	27%	0.87	4.82	4.19
ZrC/Mo FEA	44%	0.77	4.60	3.58
ZrC/Si FEA	~23%	~0.65	4.82	~3.15
HfC/W	60%	0.65	4.52	2.94
HfC/Mo	53%	0.65	4.60	2.99
HfC/Mo FEA	34%	0.88	4.60	4.05

Figure 1 shows typical I-V characteristics of a Mo emitter FEA in its initial state (stable operation in vacuum system, before deposition of ZrC film) and after deposition of the ZrC film. Note the reduction in gate voltage needed to operate the FEA at the original current levels. This voltage reduction is due to the decrease in emitter work function caused by the carbide film deposition.

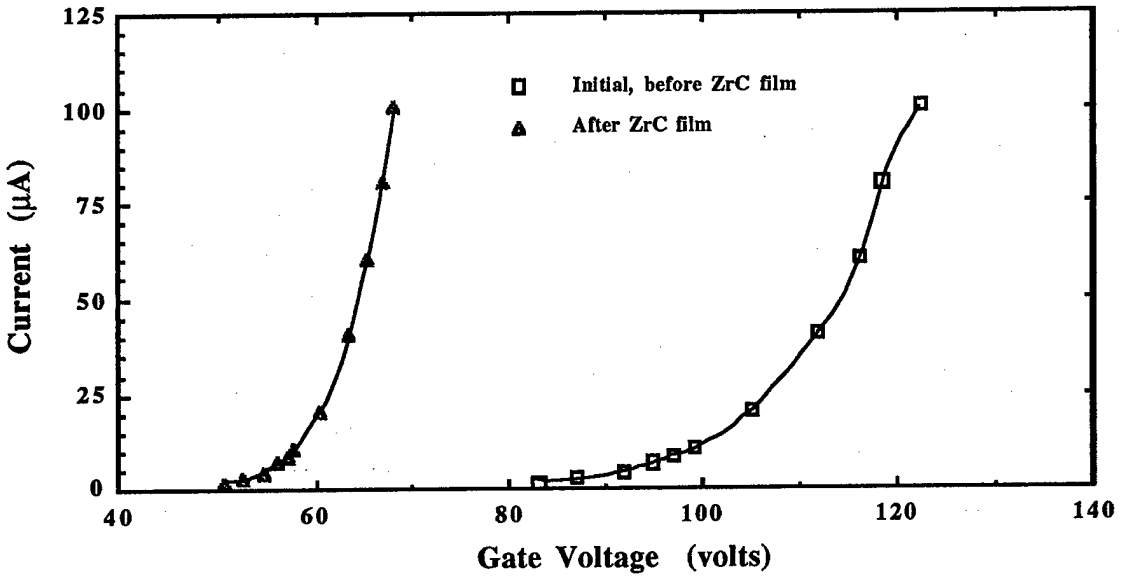


Figure 1. Comparison of emission characteristics of typical Mo emitter FEA before and after deposition of ZrC film

Another important requirement of FEAs for flat panel display applications is the ability to withstand exposure to air, for example during manufacture or storage and still be able to recover satisfactory cathode operation. We tried a variety of experiments to determine whether carbide film coatings would improve the resistance of Mo FEA emitters to air exposure. For comparison, Mo emitters are effectively destroyed (cannot be made to operate properly) after extended exposure to ambient atmosphere, probably because of oxidation of the Mo surfaces.

We began these experiments by studying the effects of atmosphere exposure on individual field emitters which were coated with carbide films. These individual emitters were not mounted in FEA structures, but were independently prepared and operated in a field emission microscope (FEM) in order that they could be carefully characterized. The geometry of the FEM was such that the applied voltage needed for operation was much higher than that used in FEAs. Nevertheless, the comparison of I-V data from Mo to carbide film, and from freshly deposited film to air-exposed film is valid. Figure 2 shows typical results of these experiments, suggesting that carbide films at least hindered the oxidation process.

A second set of experiments was conducted to determine whether it was possible to clean carbide film emitters after exposure to air. For individual emitters this is easy, because it simply requires heating. However, emitters in FEAs cannot be heated because it will damage the array structure. Therefore, we tried to use cleaning techniques which could be used on FEAs. The most successful of these techniques was to operate the emitter in a reducing atmosphere, 5×10^{-5} Torr of hydrogen for 30 minutes (hydrogen plasma). Typical results of this type of experiment are show in Fig. 3. Table II summarizes our attempts to clean these emitters by various techniques.

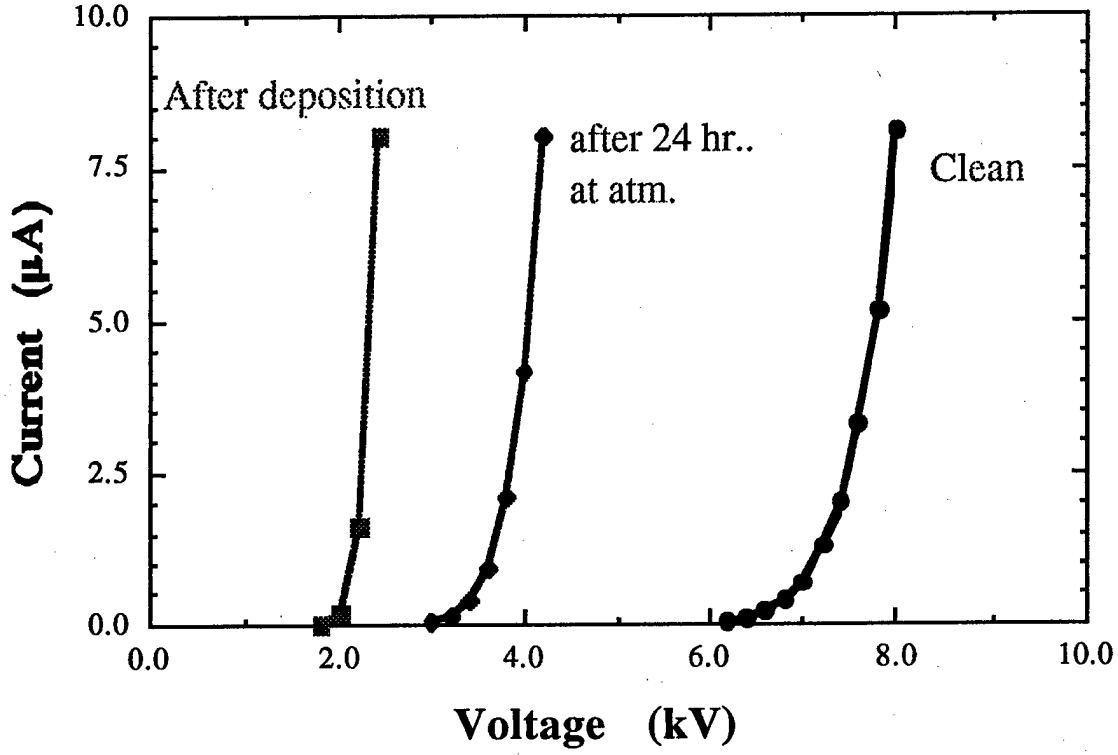


Figure. 2 Effect of atmosphere exposure on I-V characteristics of individual Mo field emitter coated with HfC film.

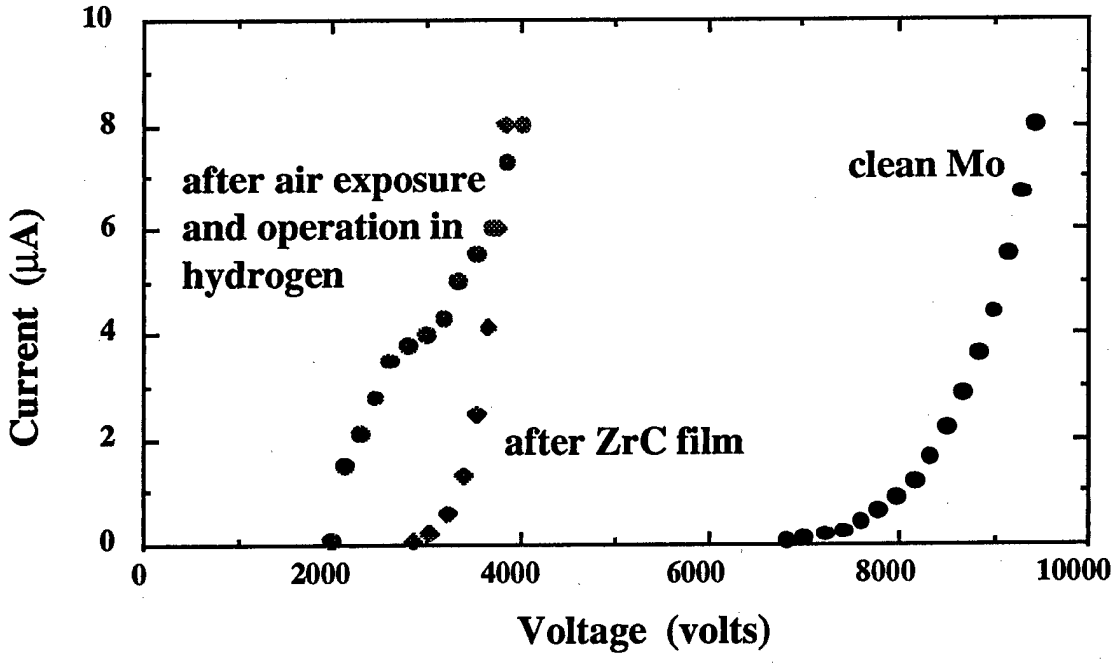


Figure 3. Effect of operation of ZrC film coated emitter in 5×10^{-5} Torr of hydrogen following atmosphere exposure.

TABLE II
Results of Emitter Cleaning Experiments

Cleaning method	Procedure	Heating temp. (°C)	Outcome
None	Cleaned Mo emitters were exposed to air (for 30 min.) prior to the deposition of the carbide film. No cleaning before deposition.	N/A	all emitters failed.
None	Cleaned Mo emitters were coated *in situ*, then exposed to air. Emission measurements taken without further emitter treatment.	N/A	mixed results short lived to fairly stable
Heating	Cleaned Mo emitters were again coated *in situ*. After air exposure the emitters were heated before data collection examination.	350	mixed results, most failed
Heating and field desorption	The above heating procedure was followed with the additional application of a desorption field. Emission measurements followed.	400	fairly stable
Hydrogen plasma	As before, cleaned Mo emitters were coated then after air exposure, the emitters were operated in 5×10^{-5} Torr of hydrogen at low currents for 30 minutes.	N/A	fairly stable to stable

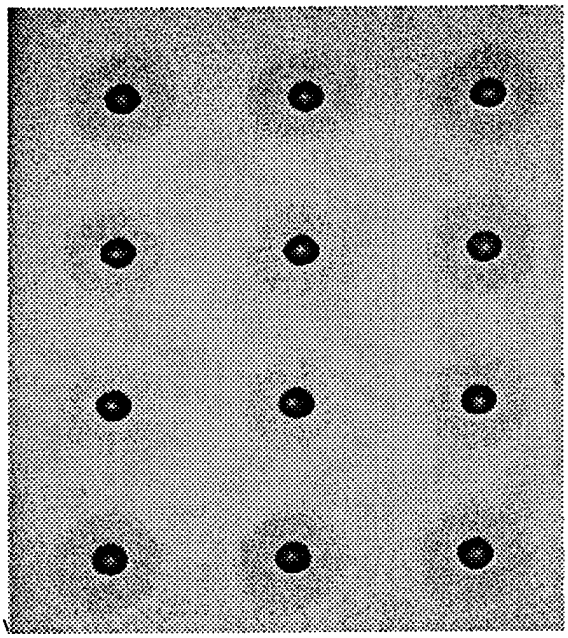
It seems that film coated emitters may be useful in FEAs for FED applications, but some issues regarding device manufacture will need to be addresses. In particular, we have identified several problems which may be encountered in the storage, handling and preparation of carbide coated FEAs. To summarize these issues, we found that cleaning before carbide deposition is important, and either avoiding subsequent exposure to air or operation of the film coated emitters in hydrogen after air exposure may also be necessary. Furthermore, carbide deposition in a system vacuum of 1×10^{-8} Torr or better may be necessary to produce optimum film performance.

B. Solid carbide emitter FEAs

A significant amount of effort was devoted to the development o FEAs with solid carbide emitter cones, rather than carbide films deposited onto Mo emitter cones. The idea was that these emitters would be tougher and more stable than the film emitters. In earlier work (not under this contract) we found that single crystal, individually fabricated carbide emitters exhibited superior characteristics compared with carbide film coated individual emitters.

There is no one who makes FEAs with solid carbide emitters. This had been tried once before by SRI but was not very successful. Fortunately, SRI was willing to work with us, combining their expertise at FEA fabrication and our expertise with the solid carbides and with the deposition of carbides. SRI provided us with a number of "blank" arrays (that is, arrays of apertures fabricated in silicon, but with no deposited emitters). We then undertook to grow solid carbide emitters in these blanks and test their operation. We also, independently of SRI, fabricated small arrays, sometimes with only a single aperture, using focused ion beam microfabrication (FIB) equipment housed at FEI Co. The time on this equipment was donated by FEI Co.

We had moderate success in preparing ZrC emitter cones in blank arrays supplied by SRI. Much effort was devoted to developing the process, including insulator, resist, and metal deposition as well as the carbide deposition itself. There was a significant amount of difficulty in getting the cones to adhere properly to the Si substrate during this process. Figure 4, for example, shows ZrC emitters deposited by the Spindt process, but they are not well centered, indicating that they have moved during wet chemical processing. Most of these problems were overcome by the end of the contract, but it was still difficult to get reproducible results.



SEM micrographs of ZrC emitters formed in a 10x10 Spindt array. The aperture diameter is ~0.8 μm. Emitters have good form but with relatively large radii (~70 nm).

Figure 4. SEM micrograph of 10x10 FEA with deposited ZrC solid carbide emitter cones.

Operation of a successful FEA with carbide cone emitters is indicated in Fig. 5. This 10x10 array of solid cones, deposited into a "blank" array provided by SRI, was able to emit about 0.05 μA per emitter at 75 V gate voltage. While this is not spectacular performance, it does demonstrate that the technology can be developed. Whether the emission and stability characteristics are superior to those of ZrC films on Mo emitter FEAs has not been determined, and awaits future work.

The FEA performed better the longer it was turned on, undoubtedly indicating that it was cleaning up during operation. We did not try hydrogen cleaning on these emitters because the large amount of effort devoted to development of the process precluded such cleaning experiments on solid emitters during the term of the contract. There are probably significant differences between the contamination described earlier in the context of carbide film coated Mo emitters and the contamination developed in the solid carbide cone emitter processing described here.

Some of the progress in development of "single arrays" for testing using the FIB technology is indicated in Figs. 6-8. Table III indicates the performance of one of these FEAs compared with a standard FEA with Mo emitters. Note that the single solid carbide emitter, with a 2 μm aperture, produced the same emission per tip as the Mo 10,000 emitter FEA, but at a lower operating voltage. The field at the emitter was significantly less, since a smaller aperture produces a higher field for the same applied voltage

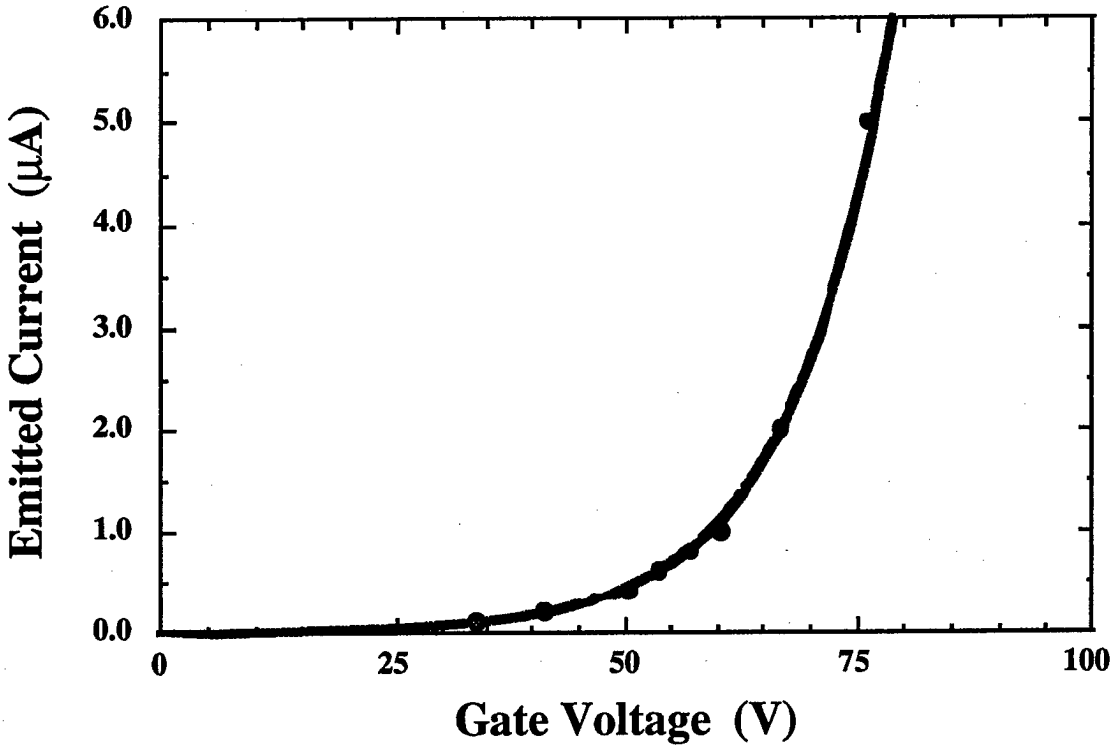
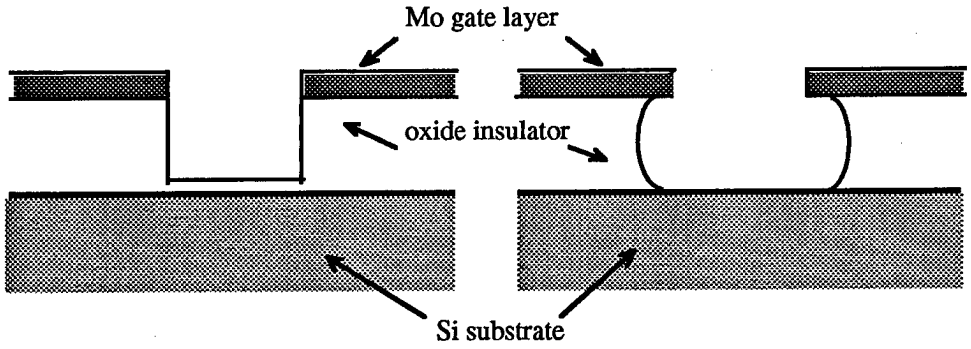


Figure 5. I-V characteristics of a 10x10 array of solid ZrC emitters deposited in "blank" FEA provided by SRI.



FIB micro-machining of individual emitter apertures.
(a) Blank array depicted here after FIB processing.
(b) Finished blank after buffered oxide etch.

Figure 6. Schematic of FIB micromachining process for individual FEA apertures prior to deposition of carbide emitter cones.

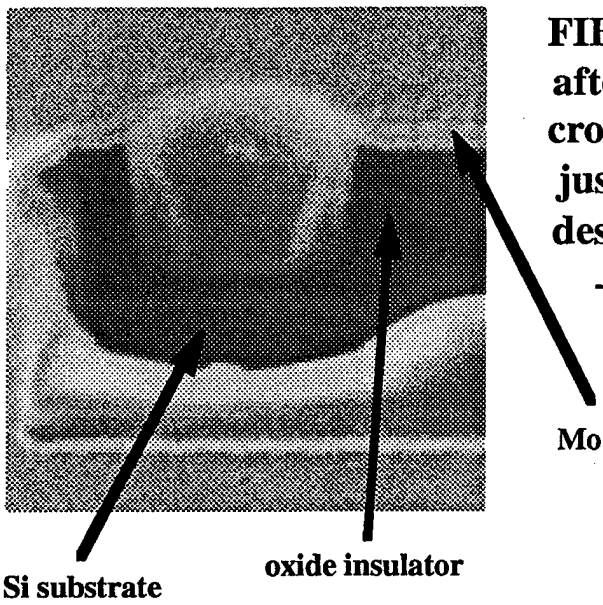
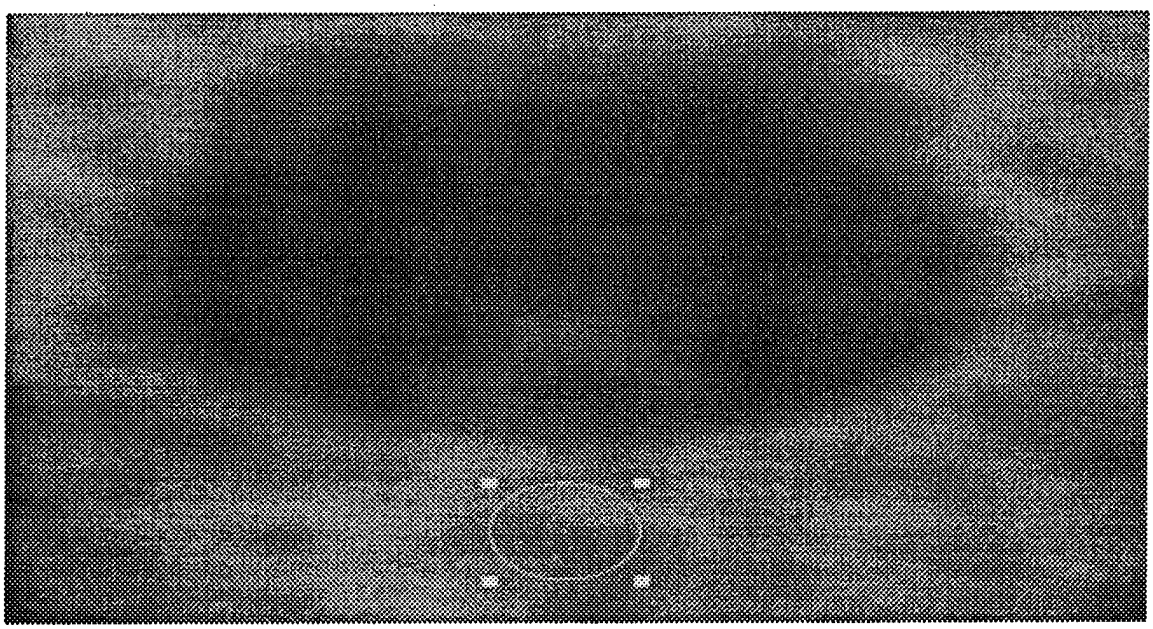


Figure 7. Image of FEA aperture fabricated by focused ion beam microfabrication (FIB).



Single ZrC cone made using FIB technology.

Figure 8. SEM image of single ZrC cone emitter in single aperture produce by FIB.

TABLE III
Comparison of Single ZrC Solid Cone Emitter FEA with Mo Emitter FEA

- Mo FEA — 120 volts
  - 0.8 μm aperture
  - 10,000 emitters
  - 0.1 μA - average current per tip
- ZrC FEA — 105 volts
  - 2.0 μm aperture
  - 1 emitter
  - 0.1 μA - total current

IV. Conclusions

The intent of this program was to investigate whether the deposition of transition metal carbides could improve the performance of field emitter array cathodes for use in field emitter flat panel displays. Both zirconium carbide and hafnium carbide were studied, either by deposition onto prefabricated arrays with molybdenum emitters (film on emitter) or by deposition into apertures in "blank" arrays , thereby forming solid emitters of the carbides. The film on emitter technique proved successful, reducing the turn-on voltage necessary for cathode operation and producing more stable emitter operation. The solid cone technique did work, but was much harder to control and make reproducible.

Since the termination of this contract, SRI has continued to work on carbide film deposition onto Mo emitter arrays. ZrC and HfC films may also be useful for other applications, including robust photocathodes for electron beam lithography, substrates for development of semiconductor devices from materials like SiC, and for cathode applications where robust, stable materials are required, such as in accelerators and free electron lasers. Further studies would be required to investigate these applications.